

Reaction of O(³P) with ClONO₂: Rate Coefficients and Yield of NO₃ Product

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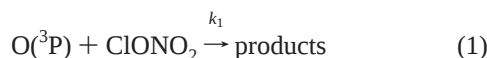
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The rate coefficient for the reaction O(³P) with ClONO₂, k_1 , was measured between 202 and 325 K using two methods: pulsed laser photolysis with time-resolved atomic resonance fluorescence detection of the O atoms and pulsed laser photolysis with long-path tunable diode laser absorption for detection of NO₃ radicals. The measured rate coefficient is summarized by $k_1 = (4.5 \pm 1.4) \times 10^{-12} \exp[(-900 \pm 80)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with $k_1(298 \text{ K}) = (2.2 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The yield of NO₃ radical in this reaction was measured to be essentially unity. Our results are compared with those from previous studies.

Introduction

Chlorine nitrate, ClONO₂, is a temporary reservoir of chlorine and, to a lesser extent, nitrogen oxides in the stratosphere. It is formed by the reaction of ClO and NO₂ in the presence of a third body. It is removed via photolysis, heterogeneous/multiphase reactions, and free-radical reactions. The rates of these processes determine the partitioning of chlorine and, to some extent, nitrogen oxides between active forms, which can destroy stratospheric O₃, and reservoir forms, which do not. The relative importance of these different processes depends on the location and season. In general, reactions of ClONO₂ with free radicals are less important than its loss via photolysis and heterogeneous reactions in the lower stratosphere. One of the free radical reactions of interest is that of O(³P) with ClONO₂:



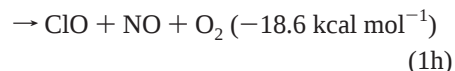
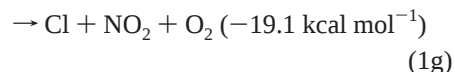
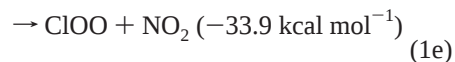
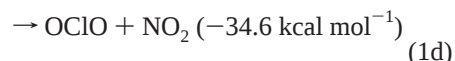
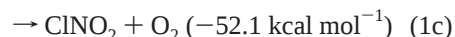
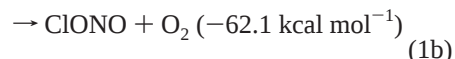
If ClONO₂ were exclusively destroyed in the stratosphere via reaction 1, its lifetime would be on the order of 30 h at 35 km in the midlatitudes ([O] = $1 \times 10^8 \text{ cm}^{-3}$). At lower altitudes, where O-atom concentrations are lower, this reaction is less important relative to photolysis and heterogeneous/multiphase reactions.

Knowledge of k_1 , the rate coefficient for reaction 1, is useful for some laboratory studies involving ClONO₂ (e.g., see ref 1) as well as in improving the database on the reactivity of ClONO₂. Therefore, k_1 was measured as a part of a larger effort in our laboratory^{2–7} aimed at understanding the atmospheric chemistry of chlorine nitrate.

The rate coefficient for reaction 1 has been previously reported at 298 K as well as at other temperatures. The currently recommended value⁸ for this rate coefficient, based on the studies of Molina et al.,⁹ Kurylo,¹⁰ and Adler-Golden and Wiesenfeld,¹¹ is $k_1(298) = 2.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with an uncertainty factor of 1.5 (i.e., it covers the range (1.3–

$3.0) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The temperature dependence of k_1 , $E/R = 900 \text{ K}$, is based on the results of Molina et al.⁹ and Kurylo,¹⁰ and the quoted uncertainty in this value is $\Delta E/R = 200 \text{ K}$.

Reaction 1 has many energetically accessible product channels:



The enthalpies of the reaction at 298 K, $\Delta H_r^\circ(298 \text{ K})$ are shown in the parentheses. This list includes channels where the products may not adiabatically correlate with the reactants. To our knowledge, only Smith et al.¹² had previously provided some information about the products of reaction 1. They suggested the products to be O₂ and ClONO to explain the end products they observed in the photodissociation of ClONO₂. Here, we report the rate coefficient for reaction 1, k_1 , as a function of temperature and the yield of the NO₃ product.

Experimental Section

Two apparatus with different detection techniques were used in this study: (1) a pulsed photolysis/atomic resonance fluorescence (PP/RF) apparatus to measure k_1 and (2) a pulsed photolysis long-path UV–vis absorption (PP/LPA) apparatus

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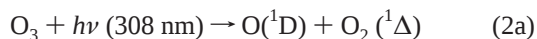
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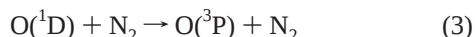
to quantify the NO₃ product yield and to measure k_1 . For ease of presentation, the two apparatus and experiments are discussed separately.

O-Atom Resonance Fluorescence. In the RF experiments, the temporal profile of O(³P), hereafter referred to as the O atom, was monitored by vacuum UV atomic resonance fluorescence. This apparatus has been described in detail elsewhere.¹³ Only a few essential details are given here. A Pyrex reactor (~150 cm³) was temperature regulated (± 1 K) by circulating methanol or ethylene glycol through its jacket. A retractable thermocouple inserted into the reaction region, defined by the volume produced by the intersection of the photolysis and probe light beams, was used to measure the temperature of the gases inside the cell.

O atoms were generated by photolyzing O₃ at 308 (XeCl excimer laser) or 532 nm (second harmonic of a Nd:YAG laser) in N₂. Photolysis of O₃ at 308 nm produces both O(¹D) and O(³P):⁸



Greater than 99% of O(¹D) was quenched to O(³P) by 15 Torr of N₂ present in the cell in less than 0.4 μs .



$k_3(298 \text{ K}) = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁸ Photolysis of O₃ at 532 nm, in the Chappuis band, leads only to O(³P):



It is known that O₂(¹ Δ) reacts with O₃ to produce O atoms.⁸ Even if O₂(¹ Δ) was formed in reaction 2c, its contribution to the measured value of k_1 should be negligible since it reacts very slowly with O₃ ($k(298 \text{ K}) = 3.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).⁸ To our knowledge, the reaction of O₂(¹ Δ) with ClONO₂ has not been studied and has no energetically allowed pathways to produce O atoms.

The fluorescence from the ³S $\rightarrow$ ³P transition (130.22–130.60 nm) of the oxygen atom, excited by the resonance lamp, was detected by a solar-blind photomultiplier tube (PMT). A calcium fluoride window mounted in front of the PMT blocked Lyman- α radiation, and the space between this window and the PMT was flushed by nitrogen. The detection sensitivity, as determined by measuring the signal level from a known concentration of O atoms, was $\sim 2 \times 10^9 \text{ atom cm}^{-3}$. (The detection sensitivity is defined as the O-atom concentration at which the signal divided by the square root of the background for a 1 s integration is unity.) A known concentration of O atoms was generated by photolyzing a measured concentration of O₃ with a laser pulse of known fluence. Approximately 10³ postphotolysis profiles were co-added to improve the signal-to-noise ratio in the temporal profile measurements. Signals 2 ms prior to the O-atom production were measured to obtain the background-scattered resonance lamp light levels.

The temporal profiles of O atoms were measured in ~ 50 Torr of He (with at least 15 Torr of N₂) under pseudo-first-order conditions in O atoms (typically $[\text{ClONO}_2]/[\text{O}]_0 > 1000$, where $[\text{O}]_0$ is the initial concentration of O atoms) with the gas mixture flowing through the reaction region at $\sim 20 \text{ cm s}^{-1}$. The gas flow velocity was sufficient to replenish the reaction region with a fresh reaction mixture between photolysis pulses. Before reaching the reactor, the gas mixture passed through two absorption cells in series (a 100 cm cell followed by a 10.6 cm

cell). Intensities (I_0) in the absence of ClONO₂ and O₃ at 213.9 (first cell) and 253.7 nm (second cell) were first measured. Then ozone was added downstream of the first cell, and its concentration was determined in the 10.6 cm cell by the attenuation of the 253.7 nm light ($\sigma_{\text{O}_3}^{253.7} = 1.16 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$). Then, ClONO₂ was added upstream of the first cell, and the attenuation of 213.9 nm light was measured to obtain the concentration of ClONO₂ ($\sigma_{\text{ClONO}_2}^{213.9} = 3.39 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$). Dilution of the O₃ due to the addition of ClONO₂ was minimal, and the ozone concentration was essentially unchanged. This negligible change was evident from the measured light intensity at 253.7 nm as ClONO₂ was added; it decreased by an amount consistent with that expected from the concentration of ClONO₂ flowing through this cell. Note that the exact concentration of O₃ was not needed, since the rate coefficients were measured under pseudo-first-order conditions in O-atom concentrations. The concentrations of both O₃ and ClONO₂ were corrected for the temperature and pressure differences between the absorption cells and the reactor. Concentrations of O₃, O(³P), and ClONO₂ were typically $3 \times 10^{14} \text{ molecule cm}^{-3}$, $6 \times 10^{10} \text{ atom cm}^{-3}$, and $(2-18) \times 10^{14} \text{ molecule cm}^{-3}$, respectively.

Long-Path Absorption (LPA) Measurements. In the LPA study, the temporal profile of NO₃ was measured by detecting the attenuation of the 662 nm radiation from a tunable diode laser. Only NO₃ contributes significantly to the changes in absorption of 662 nm light in this system after photolysis. The LPA apparatus is the same as that used in our previous study⁵ of the reaction of Cl atoms with ClONO₂. Therefore, only the aspects of the experiments relevant to the understanding of the present study are discussed here.

The concentrations of ClONO₂ and O₃ were measured in the reactor via UV absorption spectroscopy between $\sim 200-350$ nm using a 0.27 m spectrometer equipped with a CCD detector. Both ClONO₂ and O₃ have relatively unstructured absorption spectra in this wavelength region. Yet by fitting linear combinations of the reference absorption spectra of O₃ and ClONO₂ to the spectrum of the cell contents and minimizing the residual, we were able to determine the concentration of both species accurately. Using this method, we also established that, within the error of our measurements (absorbance of ~ 0.001), no other absorbing species were present in the cell, i.e., all the measured absorption was accounted for by ClONO₂ and O₃. The concentrations of O₃ and ClONO₂ were also measured in two separate absorption cells, as in the case of the RF experiments. Concentrations determined by the single-wavelength method agreed to within 10% of those measured in the reactor by the CCD. The concentrations of the cell contents were measured both before and after photolysis.

Either the D₂ lamp radiation, to analyze the cell contents by UV absorption, or the 308 nm photolysis laser beam passed through the cell at a given time. Positive position mounts allowed us to quickly and reproducibly switch the beams. The single-wavelength measurements were used to monitor any significant changes in the reactant concentrations during the acquisition of temporal profiles after the D₂ lamp beam was replaced by the laser beam.

The O(¹D) atoms produced by the 308 nm photolysis of O₃ were quickly quenched to O atoms by 200 Torr of N₂ (reaction 3). The 308 nm beam unavoidably photolyzed ClONO₂ also. To reduce the contribution of the possible reaction of ClONO₂ photolysis products with O atoms while maximizing the loss of O atoms via reaction with ClONO₂ (rather than with O₃),

the laser fluence was maintained at $<15 \text{ mJ pulse}^{-1} \text{ cm}^{-2}$ and the concentration of ClONO₂ was at least 4 times greater than that of O₃.

A beam-combining mirror, which transmitted the 662 nm diode laser beam and reflected the 308 nm photolysis beam into the cell, was used to co-propagate the photolysis and probe laser beams. The 662 nm beam was adjusted to be in the center of the photolysis beam inside the reactor. The diode laser ran single mode with an output power between 3 and 5 mW. The nominal wavelength of the diode laser was measured using a scanning monochromator. The exact wavelength of the laser need not be known because we measured the relative yields; however, it should not change during our experiments to keep the detection sensitivity the same. Therefore, the laser wavelength was locked to 662 nm, the peak of the NO₃ absorption feature, by adjusting the laser current ($\sim 50 \text{ mA}$) and temperature ($\sim 300 \text{ K}$). Even if there was a small drift (which was much less than 0.1 nm), the absorbance for a given concentration of NO₃ would not change because the absorption cross-section of NO₃ in this region, $662.0 \pm 0.1 \text{ nm}$, is essentially constant.

The intensity of the 662 nm beam passing through the reactor prior to the photolysis laser pulse was taken to be I_0 . The intensity after the laser pulse, I_t , was used with I_0 to calculate the absorbance as a function of time. Thus, we measured only absorption changes due to photolysis. From the absorbance, the concentration of NO₃ at any given time was computed using the known path length (92 cm) and the NO₃ absorption cross-section at 662 nm ($2.2 \times 10^{-17} \text{ cm}^2$).¹ The time segments for absorbance measurements varied between a few microseconds and a few milliseconds, depending on the experiments. The calculated sensitivity for NO₃ detection for one laser pulse was $\sim 1 \times 10^{10} \text{ molecule cm}^{-3}$ (absorbance of $\sim 2 \times 10^{-5}$).

The yield of NO₃ in reaction 1 and the rate constant k_1 were deduced from the same set of NO₃ profiles, which were acquired as follows. Nitrogen carrier gas was flowed through the reactor. A spectrum, I_0 , of the cell content was measured using the CCD. O₃ and ClONO₂ were added to the N₂ flow from their respective reservoirs, and a second spectrum, I_t , was recorded. Using the two spectra, the concentrations of O₃ and ClONO₂ in the reactor were determined. Necessary mirrors were repositioned to propagate the excimer and diode laser beams through the reactor. The intensity of the diode laser beam exiting the reactor was measured by a photodiode detector. The gas mixture (containing O₃ and ClONO₂) was photolyzed by the 308 nm laser beam, and the temporal profile of NO₃ absorption was recorded by monitoring the 662 nm diode laser beam. The NO₃ data acquisition was triggered $\sim 4 \text{ ms}$ before the laser pulse to obtain a background signal (I_0). Typically, 5–100 profiles were co-added to enhance the signal-to-noise ratio. The mirrors were repositioned to pass the D₂ lamp beam, and the concentrations of O₃ and ClONO₂ were remeasured. O₃ and ClONO₂ were replaced by N₂O₅, and its concentration was measured by UV absorption using the CCD, as in the case of ClONO₂ and O₃. The mixture was photolyzed by the 308 nm laser pulse, and the temporal profile of NO₃ produced was recorded. Following photolysis, the concentration of N₂O₅ was measured again. While acquiring the temporal profiles, the concentrations of N₂O₅ or O₃ and ClONO₂ were monitored via the single-wavelength measurements in absorption cells external to the reactor. The sequence of measurements was repeated at several ClONO₂ and N₂O₅ concentrations (4–8) at 298, 273, and 248 K.

Materials. Chlorine nitrate was synthesized¹⁴ by reacting Cl₂O with an excess of N₂O₅ and purified by several trap-to-

trap distillations (using three traps at 195, 159, and 78 K). The sample used in the RF study was analyzed by chemical ionization mass spectrometry (CIMS) to quantify the amount of NO₂ ($<0.05\%$), Cl₂ ($<0.2\%$), OCIO (0.05%), and Cl₂O (0.1%) impurities. The sample used in the LPA system was analyzed by UV absorption only; the levels of NO₂, Cl₂, OCIO, and Cl₂O were $<0.05\%$, $<0.5\%$, 0.5%, and $<0.5\%$, respectively. The samples were used without further purification. Chlorine nitrate was stored in the dark at 195 K. N₂O₅ was synthesized by reacting O₃ with NO₂. N₂O₅ emerging from the end was trapped in a vessel held at 195 K. The NO₂ was made via the reaction of O₂ with purified NO (higher nitrogen oxides were removed by passing NO through a silica-gel trap at 195 K). The N₂O₅, stored in a glass trap at 195 K, was eluted by a flow of N₂. The He carrier gas used in the RF study was dried by flowing it through a molecular-sieve trap held at liquid nitrogen temperature. Mixtures of ozone in the diluent gas were prepared in 12 L bulbs and used in the RF experiments. For the LPA experiments, ozone was eluted by passing dried N₂ through a silica-gel trap at 195 K that stored ozone. Such a procedure was necessary to maintain a steady high O₃ concentration at the flow velocities and pressure used in this experiment. Helium (UHP $>99.999\%$) and N₂ (UHP $>99.9995\%$) were used as supplied. The N₂ gas used for the flush between the reactor and the PMT was 99.98% pure.

Results

The data acquisition and analysis for the RF and long-path absorption experiments were different and are presented in separate sections below.

O-Atom Resonance Fluorescence. The temporal profile of O atoms in the presence of ClONO₂ following their photolytic production from O₃ was governed by the following reactions:



Reactions 4 and 5 represent O-atom loss out of the reaction zone via processes other than reaction 1 and are assumed to be first order in O-atom concentration. Reaction 4 represents reactions of O atoms with O₃ and any impurities in the gas mixture or species created by the laser photolysis; these reactions are assumed to be first order in O atoms. Orkin et al.¹⁵ have discussed how one could explicitly deal with the loss of O atoms via a combination of diffusion and reaction. In our experiments, since the loss of O atoms in the absence of ClONO₂ was essentially exponential, we simply treated this loss as a first-order process. The O-atom temporal profiles due to the above process were governed by a simple exponential decay given by

$$\ln(S_t) = \ln(S_0) - k't \quad (6)$$

where S_t and S_0 are the RF signals of O atoms at time t and 0, respectively, and

$$k' = k_1[\text{ClONO}_2] + k_5 + k_{4a}[\text{O}_3] + \sum_i k_{4i}[\text{impurity } i] \quad (7)$$

In the above expression, the contribution to the O-atom loss via reaction with O₃ is denoted by $k_{4a}[\text{O}_3]$, while the contribution due to impurities is represented by the last term in eq 7. A typical O-atom temporal profile is shown in Figure 1. The line

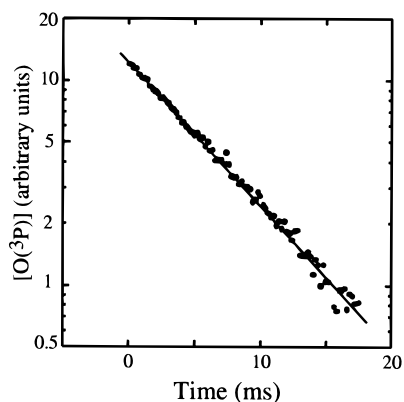


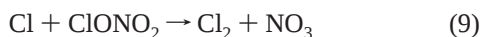
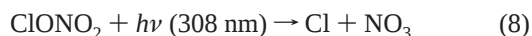
Figure 1. Temporal profile of the O-atom signal in the presence of 4×10^{14} molecule cm^{-3} of ClONO₂ at 299 K. The line is a fit of the data to eq 6.

in the figure is the linear least-squares fit of the data to eq 6. Values of k' were measured at various concentrations of ClONO₂ (shown in Table 1) to obtain k_1 from plots of k' versus [ClONO₂] using a weighted linear least-squares fit of the data to eq 7. A typical plot for k' versus [ClONO₂] at 298 K and the linear least-squares line are shown in Figure 2. The second-order rate constant k_1 was measured at 10 temperatures between 202 and 325 K.

Table 1 lists the experimental conditions and the measured values of k_1 along with the obtained precision in the plots of k' versus [ClONO₂]. The obtained values of k_1 are plotted in the Arrhenius form in Figure 3.

The fluence of the 532 nm beam was varied over a factor of 3 (20.5–64.8 mJ cm^{-2} pulse⁻¹). The measured value of k_1 was independent of laser fluence, and hence, the photoproducts of ClONO₂ could not have contributed significantly to the measured value of k_1 . As noted earlier, the expected concentrations of the products of photodissociation of ClONO₂ are so small ($<10^{11}$ cm^{-3}) that they cannot contribute significantly to the measured O-atom loss-rate coefficients. The flow rate was varied by a factor of 4 (20–80 cm s^{-1}), and the pressure was changed from 40 to 60 Torr. These experimental conditions were varied to test for systematic errors that could have affected the kinetic determination. The measured rate coefficients were invariant for the above changes, within the precision of the measurements.

Long-Path Absorption Measurements. Since both ClONO₂ and O₃ are photolyzed at 308 nm, the obtained NO₃ profiles had contributions from three sources:



Photolytic production of NO₃ from reaction 8 was essentially instantaneous. We saw no evidence for the formation of vibrationally excited NO₃ and its subsequent relaxation to the detected ground state on the time scale of our experiments.^{5,6} Recent work^{7,6,16,17} has shown that the quantum yield for NO₃ and Cl is 0.65 at 308 nm, and the O-atom yield is <0.05 . The rate constant for reaction 9 is ~ 60 times larger than that for reaction 1, such that Cl atoms are removed very rapidly compared to the O atoms. The Cl-atom loss rate is further enhanced in our experiments due to its reaction with O₃. The typical lifetime ($1/e$) for loss of Cl via reactions with ClONO₂

and O₃ was <0.25 ms in our experiments. On the other hand, the lifetime for loss of O atoms via reaction 1 was >3 ms. Thus, the contribution of reaction 9 to the measured NO₃ profile was limited to very short times. The NO₃ absorption profile, Figure 4, shows these time scales.

The NO₃ absorbance profiles after ~ 0.3 ms followed the equation:

$$\ln(A_\infty - A_t) = -k't + \ln(A_\infty - A_0) \quad (10)$$

where A_∞ is the absorbance after reaction 1 has gone to completion ($t > 0.01$ s), A_t is the time-dependent absorbance, A_0 is the absorbance by NO₃ after photolysis when reaction 9 has gone to completion, and k' is the pseudo-first-order rate constant for the loss of O atoms via reactions 1, 4, and 5. Because the loss of NO₃ was very slow on the time scale for the completion of reaction 1, A_∞ was essentially the same as the maximum absorption that was measured. (We actually accounted for the slow loss of NO₃ in the data analysis.) An example of the temporal profile of ($A_\infty - A_t$) is shown as the inset in Figure 4. A least-squares fit of this profile yielded k' , the first-order rate coefficient for the loss of O atoms. The fit was limited to times after reaction 9 had gone to $>99\%$ completion. In these experiments, loss of O atoms via process 5 is negligibly small and reaction 4 was minimized. The decays extended over 2–3 lifetimes for the O atom and were strictly exponential. The measured values of k' were plotted against the [ClONO₂] to obtain k_1 as the slope. The values of the rate coefficients obtained from the LPA experiments at 298, 273, and 248 K are included in Table 1.

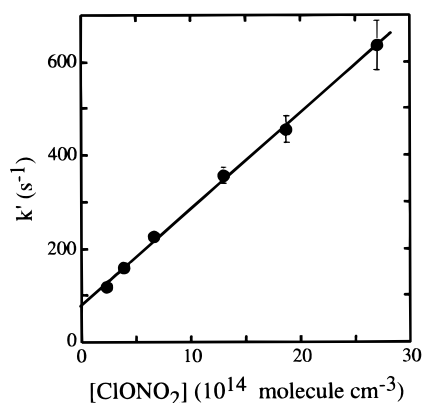
A determination of the NO₃ yield from reaction 1 required the knowledge of three quantities: (i) the initial concentration of O atoms produced, (ii) the fraction of O atoms lost via reaction with ClONO₂ (as opposed to other reactions), and (iii) the concentration of NO₃ that was generated from reaction 1a. If NO₃ was produced by reactions other than 1a, such reactions needed to be quantified and/or minimized. Of all these parameters, the initial O-atom concentration is the most difficult to obtain accurately. The O-atom concentration in our experiments was calculated from the measured concentration of O₃ (O-atom precursor), the known O₃ absorption cross-section at 308 nm, and the photolysis laser fluence by assuming the quantum yield for O-atom production in O₃ photolysis to be unity. The laser fluence was deduced from the NO₃ generated by the photolysis of ClONO₂ itself or of N₂O₅ in a separate experiment. ClONO₂ photolysis generates NO₃, and hence, the laser fluence could be derived from this NO₃ formation since the quantum yield for its formation is known. Therefore, NO₃ from ClONO₂ photolysis acted as an "internal fluence calibration".

The NO₃ temporal profiles measured after the photolysis of a mixture of O₃ and ClONO₂, such as that shown in Figure 4, were analyzed for NO₃ yield. The absorbance of NO₃ from reaction 1 was separated from that due to ClONO₂ photolysis (reaction 8), which is instantaneous on the time scale of our experiments, and reaction 9, which is complete after ~ 0.25 ms. The concentration of NO₃ generated due to reaction 1, denoted in Figure 4 by M, is clearly seen in the figure as the slowly rising signal which reached a maximum. The value of M, $A_\infty - A_0$, was obtained from the intercept, $\ln(A_\infty - A_0)$, in a plot of $\ln(A_\infty - A_t)$ versus time (inset in Figure 4) using a linear least-squares analysis. This method of obtaining the concentration of NO₃ produced in reaction 1 is referred to here as the graphical method. The concentration of NO₃ generated from

TABLE 1: Measured Values of k_1 (in $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and Experimental Conditions from Resonance Fluorescence and Long-Path Systems^a

T, K	[O] ₀ ^b	[ClONO ₂] ^c	$k_1 \pm (2\sigma \text{ precision})$	% error due to impurities ^d			total uncertainty in % ^f	$k_1 \pm (2\sigma)^e$
				NO ₂	Cl ₂ O	OCIO		
202	6	1.95–19.3	5.49 ± 0.20	10.7	3.56	0.02	12.9	5.49 ± 0.71
206	4	1.26–10.5	5.7 ± 1.1^g	10.4	3.68	0.02	23.1	5.7 ± 1.3
223	7	0.82–17.3	8.04 ± 0.40	7.0	3.13	0.02	10.4	8.04 ± 0.83
247	5	4.02–17.0	10.6 ± 0.71	5.0	2.98	0.02	10.1	10.6 ± 1.1
248	6	2.82–28.2	10.1 ± 0.92	5.2	3.15	0.02	11.9	10.1 ± 1.2
248	20	9.21–23.5	9.9 ± 1.5^h	5.3	3.22	0.03	17.1	9.9 ± 1.7
249	6	0.90–13.9	11.0 ± 0.3	4.8	2.92	0.02	8.0	11.0 ± 0.9
249	5	0.84–12.9	10.6 ± 0.7^i	5.0	3.03	0.02	10.1	10.6 ± 1.1
260	7	0.87–12.0	14 ± 1	3.7	2.51	0.02	9.8	14 ± 1
273	6	0.87–12.5	14 ± 1	3.6	2.77	0.03	9.8	14 ± 1
273	85	8.64–19.2	15 ± 3^h	3.4	2.58	0.02	21.1	15 ± 3
274	2	2.95–29.0	14.4 ± 0.9	3.5	2.71	0.03	9.2	14.4 ± 1.3
298	770	2.57–11.89	24.9 ± 0.9^g	1.9	1.83	0.02	6.7	24.9 ± 1.7
298	185	3.47–35.93	$21.5 \pm 1.0^{j,k}$	2.3	2.17	0.02	7.6	21.5 ± 1.6
298	77	4.75–19.54	$20.3 \pm 0.8^{j,k,l}$	2.4	2.25	0.02	7.2	20.3 ± 1.4
298	21	3.26–16.14	$22.7 \pm 1.5^{j,k,m}$	2.2	2.07	0.02	7.4	22.7 ± 1.6
298	54	21.9–83.6	19.1 ± 2.1^h	2.6	2.40	0.03	12.2	19.1 ± 2.3
298	70	4.21–21.4	22.7 ± 1.5^h	2.1	1.98	0.02	26.7	22.7 ± 1.7
299	35	2.34–27.0	20.5 ± 0.9^n	2.4	2.24	0.02	7.4	20.5 ± 1.52
299	13	2.8–30.2	22.7 ± 0.7^o	2.1	2.02	0.02	6.6	22.7 ± 1.49
<298>			21.8 ± 0.4					21.8 ± 2.0
325	4	0.72–9.06	28.7 ± 0.7	1.6	1.82	0.02	8.9	28.7 ± 2.6
341	2	0.76–7.46	45 ± 2^p	1.0	1.27	0.02	13.0	45 ± 5.8

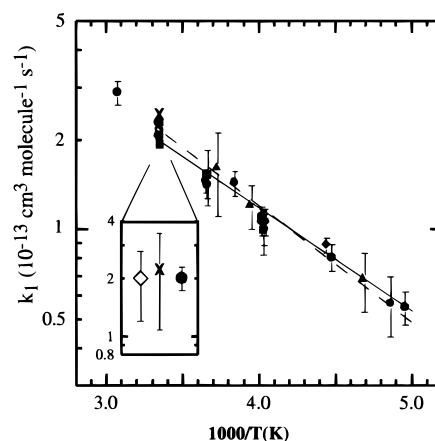
^a Unless noted, all data are from the RF experiments with the 532 nm photolysis of $\sim 3 \times 10^{14} \text{ cm}^{-3}$ of O₃ to produce O atoms. ^b In units of 10^{10} cm^{-3} . ^c In units of 10^{14} cm^{-3} . ^d These are upper limits for the contributions. ^e Added 5% uncertainty due to the uncertainty in ClONO₂ cross-section at 213.9 nm. Additional uncertainties of 1% and 11% are added to the rate coefficients at 325 and 341 K, respectively, due to the thermal decomposition of ClONO₂ and the production of NO₂. All the uncertainties were added in quadrature. ^f Errors are 2σ and include estimated systematic errors. ^g Flow rate increased by a factor of 4. ^h Data from long-path system (photolysis at 308 nm). ⁱ Laser fluence increased from 32 to 85 mJ cm⁻² pulse⁻¹. ^j 308 nm photolysis. ^k Laser fluence decreased from 11 to 3.2 mJ cm⁻² pulse⁻¹. ^l Ozone concentration reduced from 2.3×10^{15} to $7.7 \times 10^{14} \text{ molecule cm}^{-3}$. ^m Ozone concentration lowered to $2.0 \times 10^{14} \text{ molecule cm}^{-3}$. ⁿ Laser fluence = 47 mJ cm⁻² pulse⁻¹. ^o Laser fluence = 19 mJ cm⁻² pulse⁻¹. ^p Thermal decomposition affected the measurement. This value was not included in our calculation of the Arrhenius parameters.

**Figure 2.** Typical plot of k' vs $[\text{ClONO}_2]$ at 299 K. The line through the data is the linear-least-squares fit which yields $k_1 = 2.05 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

reaction 1, $[\text{NO}_3]_{\text{Rx1}}$, is given by

$$[\text{NO}_3]_{\text{Rx1}} = \frac{A_\infty - A_0}{L\sigma_{\text{NO}_3}^{662\text{nm}}} \quad (11)$$

where L is the path length through the reactor and $\sigma_{\text{NO}_3}^{662\text{nm}}$ is the absorption cross-section of NO₃ at 662 nm. The NO₃ yield in reaction 1 was obtained by comparing $[\text{NO}_3]_{\text{Rx1}}$ with the concentration of NO₃ produced via ClONO₂ photolysis and the reaction of Cl atoms with ClONO₂, shown in Figure 4 as N. NO₃ is produced from reaction 9 on a very short time scale and is essentially inseparable in our experiments from reaction 8. The quantum yield of NO₃ from the photolysis of ClONO₂ at 308 nm^{7,6} was taken to be 0.65. A fraction of the Cl atoms generated from ClONO₂ reacts with O₃ in our experiments, and this fraction was calculated using known rate coefficients for

**Figure 3.** Plot of k_1 as a function of temperature in the Arrhenius form. Work from this laboratory are 532 nm photolysis and RF detection of the O atom (●); 308 nm photolysis and RF detection (○); and 308 nm photolysis and long-path absorption detection of NO₃ (■). Also included in this plot are the findings of Molina et al.⁹ (◇), Adler-Golden and Wiesenfeld¹¹ (×, room temperature only), Kurylo¹⁰ (◆), NASA-JPL recommendation⁸ (—), and the fit to our data (---). The inset shows the room-temperature values, displaced from each other for clarity. Our value is denoted by the filled circle.

the Cl-atom reactions with ClONO₂ and O₃.⁸ This fraction was usually less than 30%, except in some experiments where it was increased to nearly 70% (see Discussion). Such analyses of 14 measurements at 298 K yielded an average value of 0.96 ± 0.17 and are listed in Table 2.

Alternatively, the entire temporal profile was fit to a reaction scheme comprised of reactions 1, 8, and 9, as well as the reaction of Cl with ozone. A commercial computer code, FACSIMILE,¹⁸ was employed to carry out such fits. For each profile, the initial concentration of ClONO₂ and O₃ were fixed

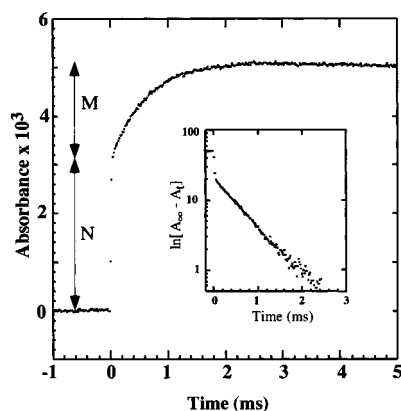
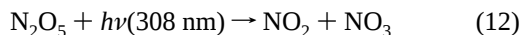


Figure 4. Temporal profile of the NO₃ absorbance following photolysis at 308 nm of a O₃ and ClONO₂ mixture ($T = 298$ K). The values of A_∞ , the amount arising from reaction 1 (M), and the amount from reactions 8 and 9 (N) are also shown. The inset shows a plot of $(A_\infty - A_t)$ on a log scale, as a function of time. A least-squares analysis of this data yielded k' as the slope and $(A_\infty - A_0)$ as the intercept. The slope was used to derive k_1 and the intercept to obtain the yield of NO₃ in reaction 1; see text for details.

at the values measured. The NO₃ radical concentration produced upon photolysis, $[\text{NO}_3]_{\text{phot}}$, was a variable in the fitting routine. The $[\text{NO}_3]_{\text{phot}}$ value obtained by the fit and attributed to the sum of reactions 8 and 9 was used to calculate the initial concentrations of O atoms, $[\text{O}]_0$, and the other photolytically produced radicals. The rate coefficient for the loss of NO₃ was assumed to be first order in NO₃ and was a variable in the model. The calculated NO₃ yield from reaction 1 was relatively insensitive ($\pm 10\%$) to changing the assigned rate coefficient for reaction 9 and the initial estimates for the three variables in the model by factors of two. The obtained results are also shown in Table 2 within parentheses.

The measured $[\text{NO}_3]_{\text{Rx1}}$, calculated from extrapolation of the temporal profiles described earlier, was also compared with $[\text{NO}_3]_{\text{Rx12}}$, the concentration of NO₃ produced by the photolysis of a known concentration of N₂O₅ at 308 nm.



These N₂O₅ photolyses were carried out before and after photolyzing ClONO₂/O₃ mixtures, without changing the laser fluence. The temporal profiles of NO₃ from N₂O₅ photolysis displayed an initial jump due to its photolytic production followed by a slow decay due to loss via reactions with impurities, such as NO₂, and a very slow diffusive loss out of the probe beam area. The NO₃ yield in reaction 1 was calculated using

$$\Phi_{\text{rxn}} = \frac{[\text{NO}_3]_{\text{Rx1}} \sigma_{\text{N}_2\text{O}_5} [\text{N}_2\text{O}_5] \Phi_{\text{N}_2\text{O}_5}}{[\text{NO}_3]_{\text{Rx12}} \sigma_{\text{O}_3} [\text{O}_3]} \quad (13)$$

where $[\text{NO}_3]_{\text{Rx1}}$ was obtained from the graphical analyses. The absorption cross-sections of O₃ and N₂O₅ evaluated at 308 nm^{19,20} are 1.34×10^{-19} and 2.46×10^{-20} cm² molecule⁻¹, respectively. The quantum yield for NO₃ from the photolysis of N₂O₅ at 308 nm was taken to be 0.96 ± 0.15 .²¹

Discussion

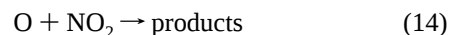
The measured values of k_1 from the LPA method agrees with those from the RF method within the precision of the measurements (Figure 3). In the RF method, the disappearance of the reactant O atom was monitored, and in the LPA method, the

appearance of the NO₃ product was measured. In both methods, ClONO₂ was much more abundant than O atoms.

Potential sources of errors in the values of k_1 measured in the RF system were (a) loss of O atoms via reaction with species other than ClONO₂, such as photoproducts and impurities in the ClONO₂ sample, (b) errors in determining the ClONO₂ concentration in the reactor, (c) precision of the measured temporal profiles, and (d) thermal decomposition of ClONO₂, which leads to reactive impurities as well as a depletion of ClONO₂. The loss in ClONO₂ due to thermal decomposition and the consequent lowering of the measured value of k_1 is quite small and was always less than a couple of percent. Yet thermal decomposition can be a major problem because it produces species, such as NO₂, that can react much faster with O atoms than ClONO₂. These errors are discussed below.

In past kinetic studies,^{9-11,17,22} short wavelength photolysis (≤ 308 nm) of various photolytes has been used to produce O atoms. However, ClONO₂ absorbs quite strongly at these wavelengths (the absorption cross-section of ClONO₂ at 308.15 nm is 1.81×10^{-20} cm² molecule⁻¹) and increases further at shorter wavelengths.² To minimize ClONO₂ photolysis, we employed 532 nm photolysis of O₃ to produce O atoms. At this wavelength, the absorption cross-section of ClONO₂ ($\ll 10^{-21}$ cm² molecule⁻¹) is so small that only a very small fraction of ClONO₂ is photolyzed. In a few experiments, O₃ was also photolyzed at 308 nm to simulate previous studies that utilized shorter wavelength photolysis for O-atom production. These 308 nm photolysis measurements also served to measure k_1 in the RF system under conditions similar to those used in the LPA system to measure the NO₃ yield. At this wavelength, ClONO₂ photolyzes to give Cl, NO₃, ClO, and NO₂.⁷ Cl atoms react rapidly with ClONO₂ to produce Cl₂ and NO₃. The rate coefficients for the reactions of O atoms with ClO, NO₂, and NO₃⁸ and the quantum yields for various photoproducts in ClONO₂ photolysis at 308 nm are known. Using this information, we calculate the maximum contribution to the removal of O atoms by the reaction of the photoproducts to be $<0.6\%$. To confirm this negligible contribution, the fluence at 308 nm was varied by a factor of 3 ($3.2\text{--}11$ mJ cm⁻² pulse⁻¹), and the measured values of k_1 did not change. Further, the obtained values agree well with those measured using 532 nm photolysis of O₃. Therefore, we are confident that our measured values of k_1 were not influenced by reactions of photoproducts.

NO₂ is an impurity in our chlorine nitrate samples, and it reacts rapidly with O atoms ($k_{14} = 6.5 \times 10^{-12} \exp(120/T)$ cm³ molecule⁻¹ s⁻¹).⁸



The contribution of this reaction to the measured O-atom profiles increases at lower temperatures where k_1 decreases while k_{14} remains nearly constant. NO₂ in our samples was not detectable via CIMS, as noted earlier. If we assume that NO₂ was present at the concentration given by the upper limits, its contribution to the measured values of k_1 would be $<3\%$ at room temperature and $<12\%$ at 202 K, the lowest temperature of this study. The contribution of OCIO to the loss-rate coefficients of the O atoms was $<1\%$ at all temperatures. Cl₂O was the only other impurity that could have reacted with O atoms.



The rate coefficient for this reaction is $k_{15} = 2.7 \times 10^{-11} \exp(-530/T)$ cm³ molecule⁻¹ s⁻¹.⁸ At the lowest temperature examined, reaction 15 contributed $<5\%$ to the measured value

TABLE 2: Summary of NO₃ Yield Data from the Long-Path UV–Vis Absorption System

<i>T</i> (K)	no. of exp	[ClONO ₂] ^a	[O ₃] ^a	[ClONO ₂]/[O ₃]	method of analysis ^b	
					internal calibration ^c	external calibration
298	14	4.21–83.6	2.94–11.8	0.5–6.5	0.96 ± 0.17 (0.93 ± 0.16)	1.13 ± 0.36
273	5	8.64–19.2	7.47–11.9	1.1–2.2	0.80 ± 0.23 (0.89 ± 0.14)	1.22 ± 0.09
248	4	9.21–23.5	3.87–4.74	1.0–5.4	0.87 ± 0.10 (0.85 ± 0.06)	1.00 ± 0.11

^a 10¹⁴ molecule cm⁻³. ^b The errors are two standard deviations of the mean of the number of measurements shown in column 2. ^c The numbers in parentheses were derived by numerical simulations (see text for details).

of *k*₁ in the RF study and at most 15% in the LPA work. Since we did not definitely measure these impurities, we did not correct our measured values of *k*₁. Instead, we have included these maximum potential contributions as uncertainties in reporting our values of *k*₁ by assuming that the presence of these impurities is uncorrelated. Strictly, the rate coefficients would only be lowered by the presence of these impurities and the error bars should be asymmetric. However, for the sake of simplicity, we have chosen to use symmetric error bounds. The systematic uncertainties due to the presence of the impurities are included in the errors quoted in the last column of Table 1. The specific contribution due to various sources and the derivation of the total uncertainties are also given in the table.

The measured concentrations of ClONO₂ are uncertain due to the uncertainties in the path length, the pressures in the reactor and the absorption cell (which was varied to check for decomposition or three-body reactions), and the UV absorption cross-sections of ClONO₂ and O₃. We evaluated these uncertainties in a previous study¹ and concluded that they add a systematic uncertainty of <5%, almost completely due to the uncertainty in the absorption cross-section of ClONO₂. By measuring the concentration of ClONO₂ via absorption in the gas flowing through a cell held at 298 K, we were able to accurately determine its concentration in the reactor, and the absorption cross-section at other temperatures was not needed.

Chlorine nitrate thermally dissociates to produce ClO and NO₂. ClO will either recombine with NO₂ or will react with itself to yield Cl₂ and O₂. Neither Cl₂ nor O₂ reacts rapidly with O atoms under our conditions. However, NO₂ reacts with O atoms rapidly enough (reaction 14) that, if present in significant concentrations, it enhances the measured values of *k*₁. To check for possible gas-phase or heterogeneous decomposition of ClONO₂, the gas flow rate was varied by a factor of 4; *k*₁ was invariant with the changes in the flow rate for *T* ≤ 325 K. Note, if ClONO₂ is lost via hydrolysis on the surface, the HNO₃ and HOCl products would not react very rapidly with O atoms.⁸ We calculate that for *T* ≤ 325, the extent of thermal dissociation of ClONO₂ for a typical residence time (~24 s) in the manifold and photolysis cell was <0.3%. Assuming this upper limit for the thermal dissociation could introduce an error of 11% to *k*₁ at 325 K; it is negligible at 298 K and below. This uncertainty is included in the errors shown in the last column of Table 1.

At 341 K we saw clear evidence for the thermal decomposition of ClONO₂. Even though the extent of thermal dissociation of ClONO₂ is calculated to be only 1.5% at 341 K, the measured rate constant was ~45% higher than that expected from an extrapolation of data assuming an Arrhenius behavior in *k*₁. The measured higher rate coefficient at 341 K is consistent with the estimated contribution due to NO₂ produced by thermal decomposition. Therefore, the Arrhenius expression given in Table 3 was calculated using data at *T* ≤ 325 K. Thermal decomposition was also seen in our study of the Cl + ClONO₂ reaction. However, because the Cl atom reacts with NO₂ much slower than with ClONO₂, the effects of thermal decomposition manifested itself as a decrease in the measured value of *k*₁₁.¹

TABLE 3: Comparison of *k*₁ (in 10⁻¹³ cm³ molecule⁻¹ s⁻¹) Measured in This Study with Those from Previous Studies and Recommendations^a

ref	<i>A</i> ^b	<i>E</i> / <i>R</i> ± ΔE / <i>R</i> (K)	<i>k</i> ₁ (298 K) ^b	<i>f</i> (298 K)	<i>T</i> range (K)
this work	4.5 ± 1.4 ^c	900 ± 80	2.20 ± 0.20		202–325
this work	4.5	900 ± 100	2.2	1.15	
11			2.3 ± 1.2		298
9	3.4 ± 0.6	840 ± 60	2.0 ± 0.8		213–295
10	1.87 ± 1.29	692 ± 167	<i>d</i>		225–273
	3.03 ± 1.56	808 ± 133			213–295
8	2.9	800 ± 200	2.0	1.5	200–300
25	3.0	808 ± 200	2.0	1.5	213–295

^a Quoted errors are 2σ from the authors. ^b Our quoted errors include estimated systematic errors in our measurements. ^c The noted error in *A* is derived by linear least-squares fitting of ln(*k*) with 1/*T*; σ_A = *A*σ_{lnA}. The *A* value from our measurements has been adjusted to reproduce *k*(298 K). ^d Kurylo did not measure *k*₁(298 K) but determined the Arrhenius parameters by measuring *k*₁ between 225 and 273 K.

Table 3 and Figure 3 show our results along with those from previous studies of *k*₁. Our results from the LPA experiments agree with those from the RF method, within the uncertainty of the measurements. It is also clear that our results are extremely close to those from studies used to derive the recommended values. Since our data agrees reasonably well with the recently recommended values, we need not restate the possible reasons for the discrepancies with the earlier data. It should be noted that in-situ measurement of the ClONO₂ concentration and quantification of the impurities are critical to obtaining an accurate value of *k*₁. Early measurements of *k*₁, for example that of Ravishankara et al.,²³ were likely hampered by problems associated with handling and quantifying ClONO₂ as well as the reactive impurities.

In Table 3, we have also listed our results in the format used by the recommendations. Combining the results of Molina et al. and Kurylo with our data leads to essentially the same value as that derived from our data alone. It is clear that because of our extensive measurements, the uncertainty in the value of *k*₁ has been significantly reduced. The larger range of temperatures in this study has helped in reducing the uncertainty in the activation energy for the reaction.

Comparison of reaction 1 with other reactions of O atoms with inorganic chlorinated compounds, Cl₂, ClBr, or Cl₂O, leading to the formation of ClO shows a rough trend with the exothermicity of the reaction. The rate coefficient for the reaction of O atoms with Cl₂O (Δ*H*_r^o(298 K) = -30 kcal mol⁻¹) is 10 times larger than *k*₁ at 298 K. The rate coefficient for the reaction of O atoms with Cl₂ (Δ*H*_r^o(298 K) = -6.3 kcal mol⁻¹) is roughly 10 times smaller than *k*₁. These large changes are mostly due to the decreasing activation energy with the increasing exothermicity of the reactions.

The NO₃ produced in the reaction can arise from pathways other than reaction 1a. Our method was incapable of directly distinguishing NO₃ production from reaction 1a from that produced via channel 1e, which leads to Cl via the rapid thermal decomposition of ClOO,^{24,8} or 1g followed by the reaction of Cl atoms with ClONO₂. Cl-atoms react very rapidly with

ClONO₂ via reaction 9 such that the rate-limiting step for NO₃ formation will be reaction 1. Thus, the measured temporal profiles of NO₃ cannot help distinguish reaction 1a from reactions 1e and 1g. We indirectly gauged the contribution of these two channels by varying the ratio of [O₃] to [ClONO₂]. In this way, the fraction of Cl atoms that reacts with O₃, rather than with ClONO₂, will change and alters NO₃ production. Changing the [ClONO₂]/[O₃] ratio by a factor of ~10 at 298 K (~2 at 273 K and ~5 at 248 K), thus changing the fraction of Cl atoms that reacted with O₃ from ~15% to ~65% at 298 K (~30 to ~50% at 273 K and ~20 to 50%), did not appreciably affect the measured NO₃ yield. Given the large uncertainty in the values of the yield, we can say that the sum of the branching ratio for channels 1e and 1g is not very large (<0.3). However, it appears channels 1e and 1g are less likely than channel 1a because the measured rate constant and its variation with temperature are consistent with that for a simple abstraction reaction.

To our knowledge, the yield of NO₃ in reaction 1 has not been measured previously. Our measured yield of NO₃ at 298 K was approximately unity. An average of the values shown in Table 2 would be 1.07 ± 0.36 , by taking an average of the internal and external calibration results. The agreement between the values obtained using ClONO₂ photolysis as the internal standard and N₂O₅ photolysis as the external standard is good considering the errors involved. On the basis of these measurements, it appears that NO₃ and ClO are the primary products of this reaction and account for at least 70% of the reaction. Obviously, we cannot rule out other minor products.

Smith et al.¹² hypothesized that reaction 1 produced O₂ and ClONO to account for the production of Cl₂, O₂, and N₂O₅ in the 302.5 nm photolysis of ClONO₂. They suggested that the photolysis of ClONO₂ produced O atoms and that the subsequent reactions of the O atoms led to these products. However, we now know that the quantum yield for the production of O atoms in the photolysis of ClONO₂ around 300 nm is <10% and that the major products are Cl + NO₃ and ClO + NO₂, with the former set being the major products.^{7,6,16,17} The subsequent reactions of Cl with ClONO₂ and the reaction of NO₃ with NO₂ (either generated by photolysis or decomposition of ClONO₂) would lead to the products observed by Smith et al. In the absence of the details of the experiments of Smith et al., it is difficult to say if their observed products could be quantitatively accounted for by the photochemistry in ClONO₂ around 300 nm that is now reasonably well understood. However, it is clear that generation of ClO and NO₃ from reaction 1 is not contrary to the end products observed by Smith et al.

It appears that the yield of NO₃ is the same at the three temperatures examined here. The invariance of the yield with temperature suggests that a majority of the reaction proceeds via abstraction and that ClO and NO₃ are the major products.

The intercepts in the plots of the first-order rate coefficients for the loss of O atoms, measured by observing NO₃ production, versus [ClONO₂] were too large (~50–350 s⁻¹) to be accounted for by the known loss processes for O atoms in the absence of ClONO₂. This intercept cannot be measured directly, i.e., in the absence of ClONO₂. Reactions such as 14 and 15 cannot account for the observed intercepts. If oxygen atoms were reacting with one or more products of reaction 1, such as NO₃, a larger intercept might be observed. However, on the basis of the calculated concentrations of the photoproducts, it appears that secondary reactions were not the cause of this large intercept. Another possibility for the larger intercept is the presence of small amounts of reactive species, such as NO₂, in the main flow of N₂. NO₂ is known to permeate into Teflon.

Therefore, to check for this, pure N₂ was used and all the Teflon tubing was replaced by glass; the intercept did not change. Thus, we are at a loss to explain this larger intercept. Yet the agreement between the values of *k*₁ measured in the LPA apparatus with that measured in the RF apparatus lends confidence to the measured yields.

This study provides a comprehensive measurement of *k*₁ and the first report of the direct determination of the products of reaction 1. However, the previous conclusion regarding the negligible contribution of reaction 1 to the lower stratospheric destruction of ClONO₂ remains unchanged. As noted in earlier papers, reaction 1 becomes a significant loss process only at higher altitudes, where the abundance of ClONO₂ is rather low.

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